



THE ROLE OF LITHIUM IN PREVENTING THE DETRIMENTAL EFFECT OF IRON ON ALKALINE BATTERY NICKEL HYDROXIDE ELECTRODE: A MECHANISTIC ASPECT

ALEXANDER A. KAMNEV

Laboratory of Structural Research Methods, Institute of Biochemistry and Physiology of Plants and Microorganisms, Russian Academy of Sciences, 410015 Saratov, Russia

(Received 29 March 1995; in revised form 28 June 1995)

Abstract—The behaviour of iron hydroxo derivatives in alkaline solutions under the conditions of battery positive electrode performance and the effect of iron hydroxo species on the latter are considered together with the specificity of the lithium cation. This specificity has been revealed, in particular, in its influence on the dissolution/crystallization kinetics of ferric hydroxide in alkaline electrolytes using Mössbauer spectroscopic measurements. The conclusion is drawn that lithium hydroxide suppresses the two main processes which lead to alkaline battery nickel hydroxide electrode degradation upon accumulation of the iron impurity during cycling, *ie*, (i) the well-known decrease in anodic oxygen evolution overpotential (equivalent to a lower efficiency of the charging process) due to electrocatalysis by iron species, and (ii) the formation of a certain ferric oxyhydroxide structure (α -FeOOH), which affects the kinetics of phase transitions in the electrode active material, *via* recrystallization of labile poorly crystallized and/or amorphous forms.

Key words: nickel hydroxide electrode, iron impurity, lithium cation, alkaline electrolytes, Mössbauer spectroscopy.

INTRODUCTION

Iron impurity has long been known to exert a detrimental effect on alkaline battery nickel hydroxide electrodes (*nhe*) of various types lowering their charging efficiency, capacity and nickel utilization factor[1–9]. This effect tends to increase with *nhe* cycling, as a result of accumulation of ferric species in the *nhe* active material (AM), particularly in its surface layers[2–7]. On the other hand, some authors have noted that there is no direct correlation between the total amount of the iron impurity in a *nhe* and the degree of its degradation[3, 8, 9], the latter being dependent on the way (and/or form) in which the iron impurity is introduced to *nhe*[7–10]. Besides that, there are even some indications about a certain improvement of the *nhe* performance when only traces of the iron impurity are present in the *nhe* AM[10], or when iron ions have been coprecipitated with nickel(II) hydroxide[11]. Moreover, iron-containing compositions including Ni–Fe alloys[12] and sintered mixtures of ferric hydroxide (among other alternative additions proposed) with oxidized *nhe* active material and a binder[13] (also in the presence of LiOH[14]) have been patented as positive electrodes for alkaline battery applications.

It has been commonly implied that the main reason for *nhe* degradation due to iron contamination is a drastic decrease in the anodic oxygen evolution overpotential at *nhe* in the presence of iron species[1–8] which is equivalent to a lowered effi-

ciency of the charging process owing to an unfavourable redistribution of the anodic current.

A special role in preventing the iron poisoning of alkaline battery *nhe* is played by lithium hydroxide which is a commonly used addition to KOH battery electrolyte[1]; numerous authors noted the detrimental effect of the iron impurity to be considerably diminished when *nhe* were cycled in a lithiated electrolyte[4, 15–16].

The aim of the present work is to correlate the behaviour of iron hydroxo species in alkaline media, the specificity of the lithium cation (revealed, in particular, in its influence on this behaviour) and the well-known detrimental effect of iron impurities on alkaline battery *nhe* in an attempt to elucidate the role of lithium in preventing the latter effect from a mechanistic viewpoint.

EXPERIMENTAL

Aqueous KOH, NaOH and LiOH electrolytes (analytical or chemical purity) used were prepared by diluting the corresponding concentrated solutions (12 M, 17 M and 5 M, respectively) up to the desired concentrations with twice distilled water. The alkalinity, as well as carbonate impurity content (1.0 ± 0.1 mol%) in the electrolytes were controlled by titration.

Synthetic goethite (α -FeOOH) was prepared by precipitation and ageing according to Ref. [17];

testing of the dried yellowish-brown powdered sample by the X-ray diffraction and *ir* spectroscopic techniques detected no ferric oxyhydroxide forms other than α -FeOOH.

Transmission Mössbauer spectra were obtained with a conventional constant-acceleration spectrometer combined with a multichannel analyser; a standard computer statistical analysis procedure was applied. All isomer shift (IS) values are given relative to sodium nitroprusside dihydrate (SNP; for α -Fe, IS = 0.258 mm s⁻¹). Other details of experimental procedures, materials, samples preparation, data acquisition and treatment have been described elsewhere[18–20].

All experiments, except where otherwise indicated, were performed at ambient temperature.

GENERAL CONSIDERATIONS, RESULTS AND DISCUSSION

*Behaviour of iron compounds under the conditions of alkaline battery *nhe* performance*

An overview of the vast literature on the behaviour of iron compounds in aqueous alkaline media (see, *eg* [18–22] and references reported therein), taking into consideration the two factors corresponding to the performance of alkaline battery *nhe*, *ie* a relatively high alkalinity ([OH⁻] being usually 4–8 M[1]) and high redox potentials, shows that all compounds containing iron in its oxidation state below +3 would be unstable under these conditions. Thus, the formation of, *eg* magnetite Fe₃O₄ considered by Mlynarek *et al.*[8] during electrochemical oxidation of Fe(III)-containing *nhe*, could have hardly been possible. Moreover, under these conditions the formation of ferrate(VI) ions can be observed[2, 13, 22].

On the other hand, ferrate(VI) easily soluble in alkaline solutions[23] is well known to be labile in these media[24–26], the more so in the presence of nickel (and cobalt) hydroxo compounds which were shown to catalyse its decomposition[27].* Another highly oxidized iron species which might in principle be formed, *eg* during ferrate(VI) decomposition[24, 28, 29], *ie* Fe(IV), was shown[30] to decompose irreversibly in alkaline solution in contact with solid phases† yielding a hydroxylated ferric species. Other possible higher oxidation states of iron (*eg*, Fe(V)[31–33] or Fe(VIII) obtained anodically in alkaline media under special conditions for the first time in late '80s[34–36] should be regarded as exotic for battery applications.‡

Hence the iron impurity in alkaline storage battery *nhe* seems most probable to exist in the ferric

state. It should be noted that the majority of diverse iron(III) hydroxo compounds are either unlikely to be formed under the conditions discussed (*vide supra*), *eg*, β - or γ -FeOOH, or unstable undergoing gradual dissolution with further recrystallization (*eg*, amorphous ferric hydroxide)[18, 21, 38–41]. The latter processes in alkaline electrolytes lead to the formation of α -FeOOH[41–44] which is thermodynamically stable in this medium[45–47]; it has also been shown to be electrochemically inactive as compared to other iron hydroxo forms[18, 48] accumulating in iron-containing electrodes during cycling in alkali[49]. Besides that, such metastable species as polynuclear ferric hydroxo complexes (as well as their monomeric form [Fe(OH)₄]⁻)[18, 50, 51] and amorphous (colloid) ferric hydroxide particles[52] may also be present at the *nhe* surface and/or in the adjacent electrolyte layers.

The effect of iron hydroxide on the physicochemical properties of alkaline battery nickel hydroxide electrodes

In an early work by Tuomi[53], the general assumption was formulated that additives to the *nhe* might exert influences not necessarily *via* the formation of an insulating layer hindering electron transport, as had earlier been proposed by Tichenor[54], but could alter the phase transition kinetics (*ie*, accelerate or slow down some certain mass transfer processes). Later, iron (oxy)hydroxides added to the alkaline battery pocket-type *nhe* active material were shown[9] to noticeably influence its phase composition upon charging.

A quantitative evaluation of the phase composition of sintered-plate *nhes* with different amounts of iron hydroxide added onto the surface by impregnation, performed by analysing the X-ray diffraction intensity ratios for peaks (100) of β -Ni(OH)₂, (001) of β -Ni(OH)₂ and β -NiOOH, as well as peak (003) of γ -NiOOH, as described earlier[20], clearly shows that the formation of the γ -phase during *nhe* electrochemical oxidation is inhibited already in the presence of *ca.* 1% Fe/Ni (Fig. 1).

Note that Novakovskii *et al.*[9] pointed to a certain similarity in the influences of cobalt and iron hydroxides on the alkaline battery pocket-type *nhe* active material consisting in the latter inhibition effect of γ -NiOOH formation. Also, Krejci *et al.*[10], on the basis of electrochemical measurements, XPS (surface) and AAS (bulk) analyses of iron-containing sintered-plate *nhes*, came to the conclusion that, in a manner similar to that of cobalt hydroxides, traces of iron hydroxides have a beneficial effect on the structure or conductivity of the *nhe* active material.

As for cobalt hydroxide, the mechanism of its activating influence on battery *nhe* has been shown[55] to be based on the formation of CoHO₂[56, 57] on the surface of nickel hydroxide crystallites. The CoHO₂ structure[58] is featured by strong interlamellar H-bonds which hinder the intercalation process of alkaline cations and water molecules into the *nhe* active material upon charging, thus yielding a highly disordered and therefore electrochemically active γ -NiOOH phase accounting for an improved *nhe* cycling efficiency[55, 57]. The determining role

* The electrochemical formation, dissolution and further decomposition of ferrate(VI) contribute to the process of iron redistribution over the *nhe* surface during cycling (*vide infra*).

† In the absence of a solid phase, iron(IV) ions were found to be stable in alkaline solutions[28, 29].

‡ Nevertheless, such highly oxidized unstable iron species have been presumed to exist as intermediate (possibly short-lived) products in anodic oxygen evolution electrocatalysis by iron hydroxo species at the *nhe*[19, 37].

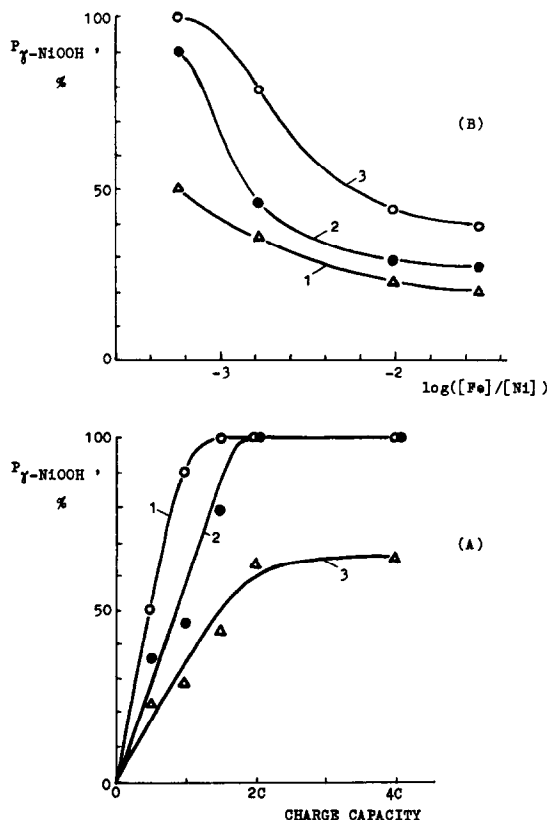


Fig. 1. Relative content of the γ -NiOOH phase in the charged sintered-plate nickel hydroxide electrode active material containing iron hydroxide added by impregnation[20] (after 7 charge-discharge forming cycles in 4.5 M KOH) as a function of: (a) the applied charge capacity at (1) $[\text{Fe}]/[\text{Ni}] = 0.06 \pm 0.01$ (natural impurity), (2) 0.17 ± 0.02 and (3) 1.0 ± 0.1 at%; (b) the Fe-to-Ni atomic ratio at applied charge capacities (1) 0.5C, (2) 1C and (3) 1.5C, where C is the electrochemical capacity equivalent to the theoretical value corresponding to the transition $\text{Ni}^{+2} \rightarrow \text{Ni}^{+3}$.

of H-bonds formed in the *nhe* active material when introducing an anionic additive, which corresponds to cobalt hydroxide by its mechanism of *nhe* activation, has been pointed out in Ref. [59].

α -FeOOH crystallizing from metastable ferric hydroxo species in alkaline media (*vide supra*) is also known to have a layered structure[60] with similar relatively strong interlamellar H-bonds[61, 62] which inhibit the intercalation of small molecules, in contrast to, *eg* γ -FeOOH[63].* Thus, from this viewpoint, α -FeOOH might well exert a similar effect on the phase transformation processes in *nhe* during charging when formed at the surface of nickel (oxy)hydroxide crystallites (*cf.* Refs. [9, 20]). Note that direct X-ray diffraction evidence for α -FeOOH formation in the active material of cycled sintered-plate *nhe* containing the iron(II) hydroxide addition

introduced by impregnation (ca. 10 mol% Fe relative to oxidized nickel) was obtained earlier[20].

It should be emphasized that the detrimental influence of iron hydroxide on phase transitions in *nhe* is noticeable at essentially smaller iron quantities[1–9, 20] than those of cobalt hydroxide which produces an activating effect[55–57], *ie*, the influence of α -FeOOH seems to be much stronger. Besides that, ferric impurity, either in the ionic form (hydroxo complexes) adsorbed at *nhe*[15, 19, 64] or as a solid (*eg*, oxyhydroxide) phase[1–10, 19, 20, 65, 66], decreases drastically oxygen evolution overpotential. Thus these two inseparable effects, intrinsic of iron hydroxo species, account for their strong summarized poisoning influence on battery *nhe*. In view of this, some positive effect of traces of iron impurity noticed by Krejci *et al.*[10] may in principle be explained. In fact, at minor iron quantities the decrease of oxygen evolution overpotential due to iron becomes negligible[65] and might well be overcompensated by the effect of the latter on *nhe* phase transitions, which in this case is similar to that of cobalt hydroxide, as was discussed earlier (see Refs. [9, 10]), yielding a well-cycling disordered electrochemically active γ -NiOOH (*cf.* Refs. [57, 59]).

Since the processes of α -FeOOH nucleation and crystallization in alkaline electrolytes take some certain time[20, 40–44, 67], it is clear why degradation of alkaline battery *nhe* upon accumulation of iron hydroxide impurity proceeds gradually[3–7], with a parallel gradual decrease in anodic oxygen evolution overpotential[20, 65] essentially contributing to this effect, and, on the other hand, why coprecipitated binary nickel-iron hydroxides having the β -Ni(OH)₂-type structure (or the α -Ni(OH)₂-type one at a higher iron content)[7, 9, 68] show a relatively good charge/discharge efficiency at primary cycling steps[9, 11, 69] with inevitable further degradation upon gradual decomposition of the binary hydroxide solid solution (including dissolution and recrystallization of the iron component).

The effect of lithium ions on the behaviour of ferric hydroxides in alkaline electrolytes

Lithium ions have been found to increase significantly the solubility (as an equilibrium thermodynamic characteristic) of α -FeOOH, as compared to that in pure NaOH or KOH electrolytes[44]. This effect (and, more generally, a solubility increase in the following sequence in KOH, NaOH and LiOH solutions) seems to be common for quite different metal hydroxides (*eg*, β -Co(OH)₂ and CoHO_2 [70], Cd(OH)_2 [71]) and may obviously be attributed to the influence of the outer-sphere cationic environment on the stability of hydroxo complexes[72–74] and, in particular cases, to the specificity of the lithium cation[73–75].

Speaking of solubility as an equilibrium thermodynamic value, only thermodynamically stable phases (such as α -FeOOH in alkaline media[45–47]) should be meant. However, as has been mentioned above, many of ferric hydroxo derivatives, being thermodynamically unstable in alkali, still may be more or less metastable. In this case, the kinetics of their transformations (in particular, dissolution

* In Ref. [63], the impossibility of intercalation of small organic molecules into the α -FeOOH phase (in contrast to γ -FeOOH) was explained by the absence of a layered structure in the former. In view of the aforementioned, we regard this explanation as erroneous.

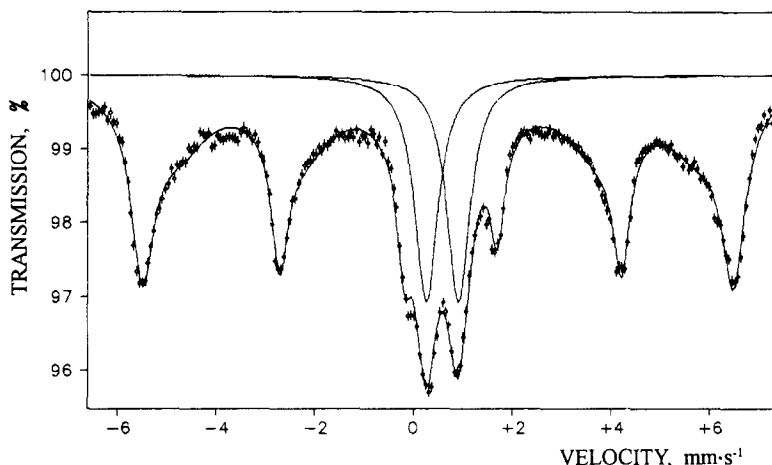


Fig. 2. Mössbauer spectrum of synthetic goethite (α -FeOOH). Central peaks represent Lorentzian-shaped components of the quadrupole doublet contributing to the overall spectrum (solid line) computer-fitted to the experimental data (points); see also Table 1 ($T = 298$ K; the same for Figs. 4–6).

and/or crystallization) may play an essential role, and the specificity of the lithium cation, as is shown below, may reveal itself.

Our previous kinetic experiments on α -FeOOH dissolution in solutions of different alkalis[21, 44], as well as on its further crystallization from highly alkaline media supersaturated with iron(III) (relative to α -FeOOH), that had been obtained by dissolving metastable and therefore more soluble amorphous ferric hydroxide, onto α -FeOOH nuclei[21] suggested the presence of such a poorly crystallized or amorphous impurity in the synthetic α -FeOOH phase used. This presumption is directly confirmed here by the presence of a central quadrupole doublet, detected in the Mössbauer spectrum of the latter phase (Fig. 2), superimposed on the characteristic magnetically split sextet of α -FeOOH. It should also be noted that the asymmetric “inward” broadening of the lines comprising the sextet (see Fig. 2) corresponds to an α -FeOOH crystallite size distribution, smaller particles giving smaller values of effective hyperfine magnetic field (H_{eff}). A computer-fitting procedure applied to the spectral data obtained here (see Fig. 2) assuming an H_{eff} distribution (with a superimposed quadrupole doublet) gives the param-

eters of the main sextet with the maximal H_{eff} (Table 1) corresponding to goethite (α -FeOOH)[76, 77]. The parameters of the central doublet shown in Fig. 2 (see Table 1) may be attributed to fine-particle goethite exhibiting superparamagnetic behaviour[76]. The latter should, however, give a magnetically split Mössbauer spectrum at liquid nitrogen temperature. Fig. 3 depicts the central part of a Mössbauer spectrum of the same sample taken at $T = 78$ K. As the central doublet observed in the room-temperature spectrum (see Fig. 2) practically disappears at 78 K, its relation to fine-particle goethite is confirmed (note that, although a similar Mössbauer behaviour in going from ambient temperature to 78 K is also observed for β -FeOOH[77], the latter phase obviously could not have formed under the synthesis conditions applied and, besides that, its noticeable quantities would have been detected by either X-ray or *ir* analyses). The remaining part still giving a weak absorption in the centre of the spectrum in Fig. 3 may be attributed to a small impurity of amorphous ferric hydroxide giving no magnetic ordering both at 298 and 78 K. Such a small relatively more highly and rapidly soluble impurity was presumed[44] to be present in synthetic α -FeOOH

Table 1. Mössbauer parameters for synthetic α -FeOOH and the product of its long-term storage in 8 M NaOH solution ($T = 298 \pm 5$ K)

Sample	Multiplicity	IS^1 (mm · s ⁻¹)	QS^2 (mm · s ⁻¹)	H_{eff}^3 (kOe)	S_r^4 (%)
Initial	Doublet	0.58 ± 0.01	0.65 ± 0.02	—	23.6
(air-dry)	Sextet ⁵	0.62 ± 0.01	0.26 ± 0.02	372 ± 6	33.1
After storage (washed, air-dry)	Sextet ⁵	0.62 ± 0.01	0.26 ± 0.02	374 ± 6	40.3

¹ Isomer shift (*vs.* sodium nitroprusside dihydrate).

² Quadrupole splitting.

³ Effective hyperfine magnetic field at ⁵⁷Fe nuclei.

⁴ Partial resonant absorption areas of spectral components which represent relative contents of the corresponding forms assuming a common recoilless fraction for all forms.

⁵ Main sextet (with the maximal H_{eff}) obtained assuming an H_{eff} distribution corresponding to crystallite size distribution.

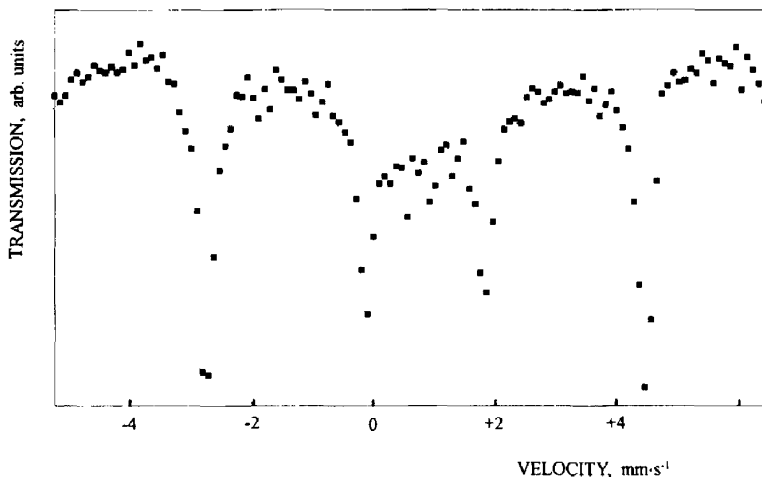


Fig. 3. Mössbauer spectrum of synthetic goethite (α -FeOOH) taken at $T = 78$ K (central part).

on the basis of its kinetic behaviour during dissolution in alkaline media.

Figure 4 shows that long-term storage of the α -FeOOH phase in 8 M NaOH or 8 M KOH solutions (1 g l^{-1} solid-to-solution ratio)* leads to practically a complete disappearance of the central spectral components featuring the poorly crystallized fractions. Although a goethite particle size distribution is also observed in this case (see the "inward" asymmetric broadening of the spectral lines in Fig. 4 similar to that of the lines comprising the sextet in Fig. 2), the spectrum is closer to that of a well-crystallized goethite[76]. The parameters of the main sextet (which is also shown in Fig. 4) obtained by statistical fitting are practically the same as for that in the initial phase (see Table 1), while its relative area is somewhat greater.

* Mössbauer spectra of the products stored in 8 M NaOH and 8 M KOH were essentially identical.

Our calculation shows that complete dissolution of more soluble metastable forms featured by the central quadrupole doublet at room temperature (see Fig. 2, Table 1), *ie*, poorly crystallized α -FeOOH particles and amorphous ferric hydroxide present in the synthetic α -FeOOH sample, would give the Fe(III) concentration in solution over $2 \times 10^{-3} \text{ M}$ which exceeds the α -FeOOH solubility by more than an order of magnitude (Table 2). Therefore it should be concluded that in 8 M NaOH (or 8 M KOH) the metastable poorly crystallized fraction undergoes complete recrystallization into goethite (most probably *via* an intermediate dissolution step[21, 44]). It is interesting to note that recrystallization obviously occurs at α -FeOOH particles of different sizes (not only at the largest crystallites featured by the main sextet; see Figs. 2, 4), which may be concluded comparing the relevant S_z values (see Table 1).

Room-temperature Mössbauer spectra of the synthetic goethite samples stored in 2 M and 4 M LiOH

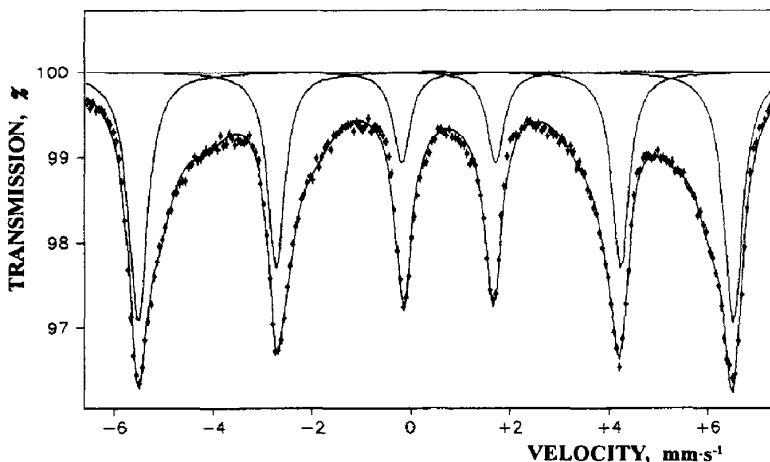


Fig. 4. Mössbauer spectrum of synthetic goethite (α -FeOOH) after its long-term storage in 8 M NaOH solution. For comparison, the Lorentzian-shaped lines are shown comprising the main magnetically split sextet (see also Table 1) which contributes to the overall spectrum (solid line) computer-fitted to the experimental data (points).

Table 2. Solubility of synthetic goethite (α -FeOOH) in alkaline electrolytes

Electrolyte	$C_{\text{Fe(III)}}^*$ (mol l^{-1})
10.0 M KOH	$(1.05 \pm 0.04) \times 10^{-4}$
8.0 M KOH	$(4.5 \pm 0.3) \times 10^{-5}$
8.0 M KOH + 0.42 M LiOH	$(6.2 \pm 0.4) \times 10^{-5}$
5.0 M KOH	$(1.3 \pm 0.1) \times 10^{-5}$
10.0 M NaOH	$(2.43 \pm 0.06) \times 10^{-4}$
8.0 M NaOH	$(1.11 \pm 0.12) \times 10^{-4}$
5.0 M NaOH	$(2.2 \pm 0.2) \times 10^{-5}$
5.0 M LiOH	$(5.2 \pm 0.2) \times 10^{-5}$
4.0 M LiOH	$(3.1 \pm 0.2) \times 10^{-5}$
2.0 M LiOH	$(7.2 \pm 1.1) \times 10^{-6}$

* Equilibrium values (reached after 2–4 months of storage at ambient temperature) obtained by analysing neutralized aliquots of centrifugated alkaline electrolytes for total iron with *o*-phenanthroline[44].

solutions clearly show that absorption in the central region is still essential even after *ca.* 4 years of storage (Fig. 5). A similar spectrum with a noticeable absorption in the central region is obtained after a *ca.* 4-year storage in mixed 8 M KOH + 0.42 M LiOH solution* (Fig. 6; only a central part of the

* Similar lithiated electrolytes are commonly used in storage batteries[1].

spectrum is shown). These results indicate that LiOH inhibits the transformation of poorly crystallized ferric forms into goethite. As this transformation obviously includes two steps, *viz.* dissolution and crystallization, it is rather the former one that is inhibited in the presence of LiOH. This directly follows from our earlier kinetic experiments which have shown that the rate of α -FeOOH crystallization from alkaline solutions, supersaturated with iron(III) (relative to the α -FeOOH phase), increases in the following sequence: KOH–NaOH–LiOH (viscosity taken into account)[21].

Note that, considering the relative absorption intensities in the central regions of Figs. 5(a) and 5(b), for 4 M LiOH the inhibition is more clearly manifested than for 2 M LiOH, in spite of the considerably lower α -FeOOH solubility in the latter case (see Table 2). Assuming the total amount of the poorly crystallized species present in the initial synthetic goethite sample (see Fig. 2) to be 100% and that in the sample stored in 8 M NaOH (see Fig. 4) to be close to zero, our estimation from the spectral data shown in Figs. 2, 4–6 gives the following “residual” amounts of the poorly crystallized species for the samples stored in 4 M LiOH, 2 M LiOH and (8 M KOH + 0.42 M LiOH) electrolytes: 24, 17 and 24% of the initial amount, respectively.

Considering the abnormal tendency of $[\text{Li}_{\text{aq}}]^+$ cations to form ion associates[73–75], it may be assumed that at higher LiOH concentrations (and,

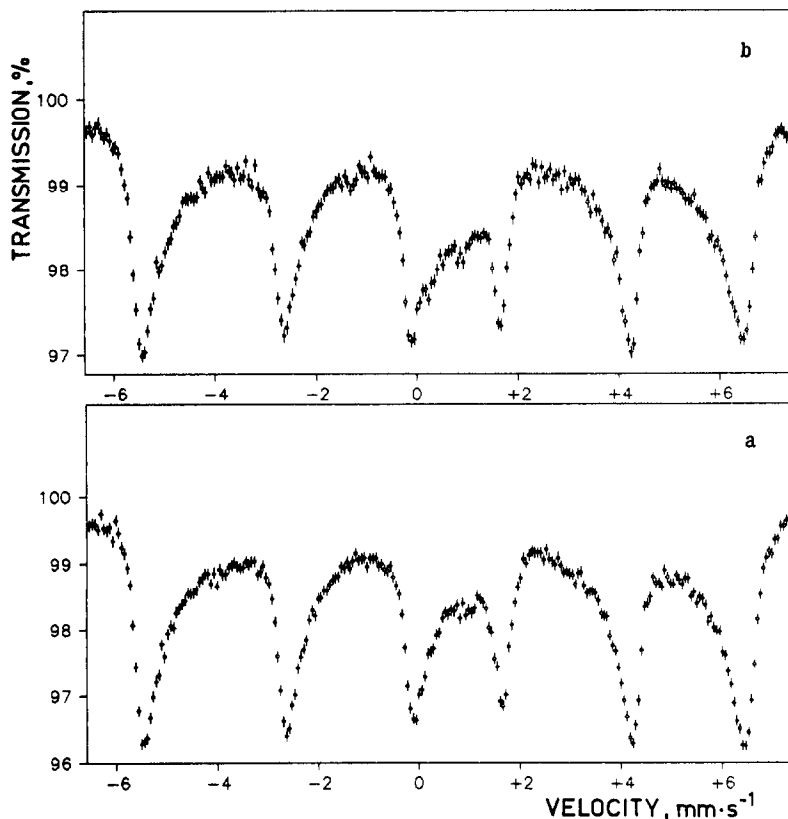


Fig. 5. Mössbauer spectra of synthetic goethite (α -FeOOH) after its long-term storage in (a) 2 M LiOH and (b) 4 M LiOH solutions.

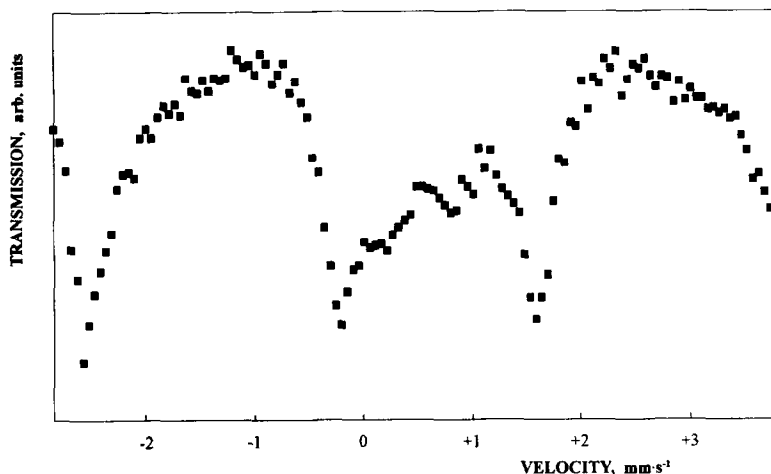


Fig. 6. Mössbauer spectrum of synthetic goethite (α -FeOOH) after its long-term storage in mixed 8 M KOH + 0.42 M LiOH electrolyte (central part).

the more so, in lithiated alkaline electrolytes where $[\text{Li}^+]_{\text{total}} \ll [\text{OH}^-]_{\text{total}}$, as in the mixed KOH + LiOH solution used here) an essential part of lithium cations is present in the form of $[\text{LiOH}]_{\text{aq}}$ associates. Comparing the data for different alkaline solutions presented above, it may be supposed that the inhibition of the dissolution step is due rather to the associated LiOH form than to lithium cations, although this requires further direct confirmation.

The detailed mechanism of the inhibition of the dissolution step still remains unclear. It may obviously involve some "superficial" interaction between the solid phase and lithium ions (or $[\text{LiOH}]_{\text{aq}}$ associates) similar to that presumed in the case of binary nickel(II)-zinc hydroxides stored in LiOH solutions, which also exhibited an anomalous behaviour (as compared with *eg*, KOH)[78, 79], showing a drastic decrease in the solubility of the zinc component from the maximal value after some "induction period"[79].

GENERAL CONCLUSIONS

In view of the aforementioned, it can be concluded that lithium hydroxide, both as pure LiOH and as an additive to, *eg* KOH solutions, affects the phenomena which accompany accumulation of iron impurity in battery *nhe* during cycling, *ie* it prevents (or lessens considerably) both the reduction of oxygen evolution overpotential (thus improving the charging current distribution) and the formation of the α -FeOOH structure by hindering the dissolution process (which is followed by recrystallization) of poorly crystallized ferric (oxy)hydroxide forms, thus providing for a better *nhe* phase transition kinetics and a higher nickel utilization factor.

It should also be noted that, in our opinion, the interpretation of the positive effect of lithium against *nhe* poisoning by iron (or its soluble species) proposed in the well-known review paper[80], consisting in the formation of a physical (*ie*, phase) barrier

preventing iron ions penetration into the *nhe* crystal lattice, does not conform to experimental facts reported in the literature cited (see *eg*, [5–9, 20] where ferric hydroxide localized at (or added to) the *nhe* surface was shown to exert even a stronger detrimental effect) and must therefore be reconsidered.

Acknowledgements—The author is pleased to thank Professor Yuri D. Perflyev and Dr Nikolai S. Kopelev (Department of Chemistry, Moscow State University, Russia), Drs Venelin Angelov and Ventsislav Rusanov (Department of Physics, Sofia University, Bulgaria) for their hospitality and encouragement, many valuable discussions and kind skilful help in experimental work, without which this study would have been much more difficult. Technical assistance of Dr Alexander D. Iosipenko (IBPPM RAS, Saratov, Russia) is also greatly appreciated. This work was supported in part by The International Science Foundation (G. Soros Foundation).

REFERENCES

1. S. U. Falk and A. J. Salkind, *Alkaline Storage Batteries*. J. Wiley & Sons, New York (1969).
2. G. Troilius and G. Alfelt, in *Power Sources. Proc. 5th Internat. Symp.*, Brighton, England, 1966, p. 337. Pergamon Press, Oxford (1967).
3. L. V. Vesheva, I. B. Shcherbakova and O. I. Bondarenko, in *Akkumulyatory. Sbornik Rabot NIAI* (Accumulators. Collection of Papers of Scientific Research Battery Institute; in Russian), p. 10. TsINTI (Central Institute of Scientific & Technical Information), Moscow (1961).
4. K. Sugita and S. Ohkuma, in *Int. Soc. Electrochem. 23rd Meet.*, Stockholm, 1972. Extend. Abstrs, p. 467 (1972).
5. A. M. Novakovskii and V. N. Drobyshvskii, in *Sbornik Rabot po Khim. Istochnikam Toka* (Collection of Papers on Chemical Current Sources; in Russian). No. 7, p. 155. Energiya, Leningrad (1972).
6. A. M. Novakovskii, N. Yu. Uflyand, M. P. Yashkov and Yu. A. Kuz'min, *Elektrotekh. Promyshlennost'. Ser. Khim. i Fiz. Istochniki Toka*, No. 1(58), 16 (1978).
7. N. Yu. Shibaeva, A. M. Novakovskii and M. P. Yashkov, in *Khimicheskie Istochniki Toka* (Chemical

- Current Sources; in Russian), p. 31. Energoatomizdat, Leningrad (1983).
8. G. Mlynarek, M. Paszkiewicz and A. Radniecka, *J. appl. Electrochem.* **14**, 145 (1984).
 9. S. M. Rakhovskaya, L. A. Paikina, B. B. Ezhov, L. A. Vereshchagina, N. Yu. Shibaeva and A. M. Novakovskii, in *Issled. v Oblasti Priklad. Elektrokhimii* (Investigations in the Field of Applied Electrochemistry; in Russian), p. 23. Saratov University Press, Saratov (1984).
 10. I. Krejci, J. Mrha, B. Folkesson and R. Larsson, *J. Power Sources* **21**(No. 2), 77 (1987).
 11. S. Yamashita and Y. Morioka, Pat. 57-37109 of Japan, cl. H 01 m 4/28, applied Dec. 5, 1974, No. 49-140298; publ. Aug. 7, 1982. Cited from *Ref. Zhurn. Energ.* (U.S.S.R.), 3F 91P (1984).
 12. P. A. C. Jacquier, English Pat. No. 708736, patented May 12, 1954. Cited from *Ref. Zhurn. Khim.* (U.S.S.R.), No. 16, 51543P (1956).
 13. E. M. Jost, US Pat. 3,615,833; US cl. 136/28, 136/12OR; Internat. cl. H 01 n 43/04; application No. 630,272, filed Apr. 12, 1967, patented Oct. 26, 1971. Abstracted in *Chem. Abstr.* **76**(No. 6), 30173v (1972).
 14. U. Von Sacken, US Pat. 5,180,574; US cl. 423/594, Internat. cl. C 01 b 6/24; application No. 828,772, filed Jan. 30, 1992; publ. Jan. 19, 1993. Cited from *Ref. Zhurn. Khim.* (U.S.S.R.), 17L 174P (1994).
 15. R. D. Armstrong, G. W. D. Briggs and M. A. Moore; *Electrochim. Acta* **31**, 25 (1986).
 16. A. K. Sood, *J. electrochem. Soc.* **136**, 372C (1989).
 17. S. Umeki, Appl. No. 56-50122 of Japan, cl. C 01 g 49/02, applied Oct. 2, 1979; publ. May 7, 1981. Cited from *Ref. Zhurn. Khim.* (U.S.S.R.), 13L 105P (1982).
 18. A. A. Kamnev, B. B. Ezhov, N. S. Kopelev, Yu. M. Kiselev and Yu. D. Perfilov, *Electrochim. Acta* **36**, 1253 (1991).
 19. A. A. Kamnev and B. B. Ezhov; *Electrochim. Acta* **37**, 607 (1992).
 20. B. B. Ezhov, O. G. Malandin, A. V. Vasev, A. A. Kamnev and G. V. Suchkova; *Elektrokhimiya* **23**, 565 (1987).
 21. A. A. Kamnev and B. B. Ezhov, *Zhurn. Prikl. Khimii* **61**, 1464 (1988).
 22. B. B. Ezhov, A. A. Kamnev, O. G. Malandin and A. V. Vasev, *Elektrokhimiya* **23**, 997 (1987).
 23. G. W. Thompson, L. T. Ockerman and J. M. Schreyer, *J. Amer. Chem. Soc.* **73**, 1379 (1951).
 24. J. Tousek, *Coll. Czechosl. Chem. Commun.* **27**, 908 (1962).
 25. H. Goff and R. K. Murmann, *J. Amer. Chem. Soc.* **93**, 6058 (1971).
 26. T. Ernst, M. Wawrzenczyk, M. Cyfert and M. Wronska, *Bull. Acad. pol. sci. Ser. sci. chim.* **27**, 773 (1979).
 27. J. Vepřek-Šiška and V. Ettel, *Chem. Ind.* **13**, 548 (1967).
 28. Yu. M. Kiselev, N. S. Kopelev and Yu. D. Perfilov, *Zhurn. Neorgan. Khimii* **32**, 2982 (1987).
 29. N. S. Kopelev, Yu. D. Perfilov and Yu. M. Kiselev, *J. Radioanal. Nucl. Chem. Articles* **162**, 239 (1992).
 30. C. Fierro, R. E. Carbonio, D. Scherson and E. B. Yeager, *Electrochim. Acta* **33**, 941 (1988).
 31. I. G. Kokarovtseva, I. N. Belyaev and L. V. Semenyakova, *Uspekhi Khimii* **41**, 1978 (1972).
 32. W. Levason and C. A. McAuliffe, *Coord. Chem. Rev.* **12**, 151 (1974).
 33. G. Demazeau, B. Buffat, M. Pouchard and P. Hagenmuller, *Z. anorg. allg. Chem.* **491**(No. 8), 60 (1982).
 34. Yu. M. Kiselev, N. S. Kopelev, V. I. Spitsyn and L. I. Martynenko, *Dokl. Akad. Nauk SSSR* **292**, 628 (1987).
 35. Yu. D. Perfilov, N. S. Kopelev, Yu. M. Kiselev and V. I. Spitsyn, *Dokl. Akad. Nauk SSSR* **296**, 1406 (1987).
 36. N. S. Kopelev, Yu. D. Perfilov and Yu. M. Kiselev, *J. Radioanal. Nucl. Chem. Articles* **157**, 401 (1992).
 37. A. A. Kamnev, B. B. Ezhov, V. Rusanov and V. Angelov, *Surf. Interface Anal.* **19**, 577 (1992).
 38. J. D. Bernal, D. R. Dasgupta and A. L. Mackay, *Clay Miner. Bull.* **4**(No. 21), 15 (1959).
 39. K. Wefers, *Ber. Dtsch. keram. Ges.* **43**, 677 (1966).
 40. O. P. Krivoruchko, B. P. Zolotovskii, R. A. Buyanov, A. Solcova and J. Subrt, *Z. anorg. allg. Chem.* **B504**, 179 (1983).
 41. G. W. van Oosterhout, *J. Inorg. Nucl. Chem.* **29**, 1235 (1967).
 42. A. M. van der Kraan and J. Medema, *J. Inorg. Nucl. Chem.* **31**, 2039 (1969).
 43. A. N. Christensen, P. Convert and M. S. Lehmann, *Acta Chem. Scand.* **A34**, 771 (1980).
 44. A. A. Kamnev, B. B. Ezhov, O. G. Malandin and A. V. Vasev, *Zhurn. Prikl. Khimii* **59**, 1689 (1986).
 45. D. Langmuir, U.S. Geol. Surv., Prof. Pap. No. 650-B, 180 (1969).
 46. T. Misawa, *Corros. Sci.* **13**, 659 (1973).
 47. D. G. Lewis and U. Schwertmann, *J. Colloid Interface Sci.* **78**, 543 (1980).
 48. I. Suzuki, Y. Hisamatsu and N. Masuko, *J. electrochem. Soc.* **127**, 2210 (1980).
 49. H. Neugebauer, W. Tschinkel, P. Federspiel, G. Nauer and A. Neckel; in *41st Int. Soc. Electrochem. Meeting, Prague, 1990. Proc.*, Vol. 2. Abstract No. Fr-88 (1990).
 50. A. E. Danilina and N. M. Pavlov, *Zhurn. Neorgan. Khimii* **26**, 420 (1981).
 51. A. A. Kamnev, B. B. Ezhov and O. G. Malandin, *Koord. Khimii* **14**, 25 (1988).
 52. M. M. Kushnir, *Ukr. Khim. Zhurn.* **23**, 813 (1957).
 53. D. Tuomi, *J. electrochem. Soc.* **112**, 1 (1965).
 54. R. L. Tichenor, *Ind. Eng. Chem.* **44**, 973 (1952).
 55. B. B. Ezhov, O. G. Malandin and S. M. Rakhovskaya, *Elektrokhimiya* **20**, 140 (1984).
 56. K. Nakamitsu, H. Yasuda, K. Iwai and K. Asada, *GS News* **43**(No. 2), 30 (1984).
 57. B. B. Ezhov and O. G. Malandin, *J. electrochem. Soc.* **138**, 885 (1991).
 58. Yu. D. Kondrashev and N. N. Fedorova, *Dokl. Akad. Nauk SSSR* **94**, 229 (1954).
 59. V. M. Rozovskii, T. I. Taldykina and B. B. Ezhov, in *Issledovaniya v Oblasti Prikladnoi Elektrokhimii* (Investigations in the Field of Applied Electrochemistry, in Russian), p. 52. Saratov University Press, Saratov (1989).
 60. T. Misawa, K. Hashimoto and S. Shimodaira, *Corros. Sci.* **14**, 131 (1974).
 61. K. J. Gallagher and D. N. Phillips, *Trans. Faraday Soc.* **64**, 785 (1968).
 62. L. Verdonck, S. Hoste, F. F. Roelandt and G. P. van der Kelen, *J. Mol. Struct.* **79**, 273 (1982).
 63. G. R. Desiraju and M. Rao, *Mater. Res. Bull.* **17**, 443 (1982).
 64. A. A. Kamnev, B. B. Ezhov, V. Rusanov and V. Angelov, *Electrochim. Acta* **37**, 469 (1992).
 65. D. A. Corrigan, *J. electrochem. Soc.* **134**, 377 (1987).
 66. S. I. Cordoba, M. Lopez Teijelo and V. A. Macagno, *Electrochim. Acta* **32**, 1783 (1987).
 67. T. Morishita and A. Kotsu, appl. 57-111245 of Japan, cl. C 01 g 49/02, H 01 f 1/10. Applied Dec. 29, 1980, No. 55-187600, published July 10, 1982. Cited from *Ref. Zhurn. Khim.* (U.S.S.R.), 19L 163P (1983).
 68. L. A. Vereshchagina, L. A. Paikina, S. M. Rakhovskaya, R. E. Tugushev, V. S. Borinskaya and I. Ya. Gvozdyukov, *Zhurn. Neorgan. Khimii* **31**, 2466 (1986).
 69. A. M. Novakovskii, T. K. Teplinskaya and N. Yu. Uflyand, in *Sbornik Rabot po Khimicheskim Istochnikam Toka* (Collection of Papers on Chemical Current Sources, in Russian), No. 10, p. 204. Energiya, Leningrad (1975).
 70. B. B. Ezhov and A. A. Kamnev, *Zhurn. Prikl. Khimii* **56**, 2346 (1983).

71. Yu. I. Ob'edkov, L. A. L'vova and I. A. Kazarinov, *Elektrokhimiya* **11**, 1247 (1975).
72. M. Z. Ugorets, *Zhurn. Fiz. Khimii* **51**, 1235 (1977).
73. B. B. Ezhov and A. A. Kamnev, *Zhurn. Fiz. Khimii* **57**, 2846 (1983).
74. B. B. Ezhov, A. A. Kamnev and O. G. Malandin, *Koord. Khimiya* **14**, 30 (1988).
75. F. Guillaume, M. Perrot and W. G. Rotschild, *J. Chem. Phys.* **83**, 4338 (1985).
76. E. Murad, *Amer. Miner.* **67**, 1007 (1982).
77. M. J. Rossiter and A. E. M. Hodgson, *J. Inorg. Nucl. Chem.* **27**, 63 (1965).
78. A. A. Kamnev and B. B. Ezhov, *Zhurn. Prikl. Khimii* **61**, 1469 (1988).
79. B. B. Ezhov and A. A. Kamnev, *Zhurn. Prikl. Khimii* **65**, 544 (1992).
80. P. Oliva, J. Leonardi, J. F. Laurent, C. Delmas, J. J. Braconnier, M. Figlarz, F. Fievet and A. de Guibert, *J. Power Sources* **8**(No. 2-3), 229 (1982).